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Group-selective enrichment and determination of pyrethroid insecticides in aquaculture seawater via molecularly imprinted solid phase extraction coupled with gas chromatography-electron capture detection

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ABSTRACT

Two types of molecularly imprinted polymers (MIPs) for the simultaneous determination of six pyrethroid insecticides have been developed using deltamethrin (D-MIPs) and cypermethrin (C-MIPs) as template molecules. A comparison of the performance of D-MIPs, C-MIPs, and the corresponding non-imprinted polymers (NIPs) were conducted. Stronger group-selective interactions between the C-MIPs and the six pyrethroid insecticides were achieved. The MISPE method based on the C-MIPs displayed higher extraction recoveries (86.4–96.0%) with RSD values ranging from 2.4 to 7.8% for the six pyrethroid insecticides in aquaculture seawater. After the C-MIP cartridge procedure, the limits of detection and quantification for fenvalerate, deltamethrin, cypermethrin, cyfluthrin, and bifenthrin were in the 16.6–37.0 and 55.3–109.1 ng L^{-1} ranges, respectively, and 0.68 and 2.26 μg L^{-1} for phenothrin, respectively. The proposed MISPE method coupled with gas chromatography-electron capture detection was successfully used for the determination of the six pyrethroid insecticides in aquaculture seawater.

1. Introduction

Pyrethroid insecticides are extensively used for pest control in aquaculture areas because of their relatively low mammalian toxicity and environmental persistence. However, because of their widespread usage and high hydrophobicity, pyrethroid insecticides are usually adsorbed into the sediment, resulting in low residue concentration in water and accumulation in marine products. Some of the pyrethroid insecticides exhibit high toxicity to fish and invertebrates at trace concentrations in both seawater and sediment. This toxicity has been linked to disruptions in the endocrine system, which can adversely affect reproduction and sexual development, as well as the immune system [1–4]. Therefore, in monitoring pyrethroid insecticides in aquaculture seawater, sensitive analytical methods that have low solvent consumption and are sensitive to trace levels of pesticide residues in aquaculture seawater must be employed.

Pyrethroid insecticides are usually determined using gas chromatography coupled with electron-capture detection (GC-ECD), mass spectrometry (GC–MS), or liquid chromatography–electrospray ionization mass spectroscopy (LC–MS) [5–7]. The MS instruments exhibit high selectivity and sensitivity; however, high costs were needed [8]. GC-ECD exhibits sufficient sensitivity and selectivity, as well as lower costs compared to MS, for many pyrethroid insecticides because of the one or more halogenated atoms present in their structures [9]. However, positive errors may occur because of the effect of complicated matrices. Therefore, cleanup steps are necessary to remove the coextracted matrix of interference and improve the selectivity of the GC-ECD analysis. Several pretreatment methods, such as solid phase extraction (SPE) [10], stir bar sorption extraction (SBSE) [11], liquid-phase microextraction (LPME) [12], solid-phase microextraction (SPME) [13], and liquid–liquid extraction (LLE) [14], have been widely used. However, SBSE, LPME, and SPME need long equilibrium times and strict experimental control and they have low sensitivity, thus limiting their application in large-scale analyses [11–13,15]. Liquid–liquid extraction is a conventional and effective isolation technique used for water samples, but emulsions limit its application [14]. Molecularly imprinted solid phase extraction (MISPE) based on selective molecularly imprinted polymers (MIPs) has been used for the isolation and clean-up of pyrethroid insecticides in different matrix samples [16,17]. However, most reported MIPs for pyrethroid insecticides were used for isolation and purification of single target analyte. Meanwhile, the concentrations of pyrethroid insecticides residues were usually low in aquaculture seawater samples.

Therefore, the objective of the present study is to develop a new MIPs with group-selectivity and good enrichment capability

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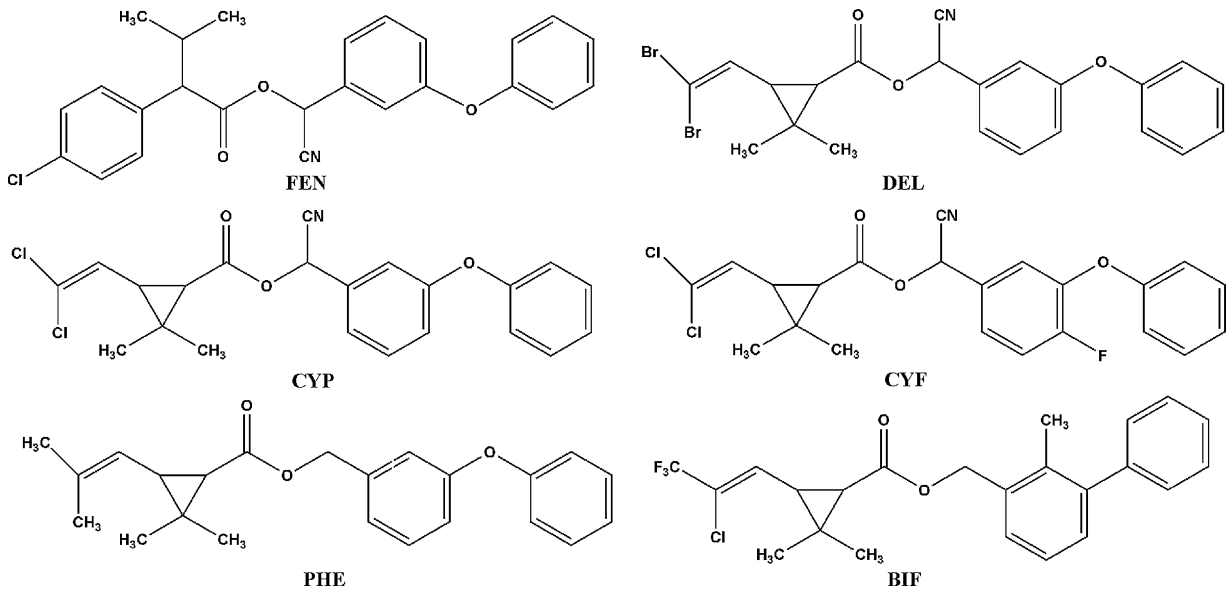

Fig. 1. Chemical structures of pyrethroid insecticides.

targeted to six pyrethroid insecticides and use it as a specific sorbent of SPE for directly enrichment and purification of pyrethroid insecticides from aquaculture seawater samples. The performance of multi-residue analytical method for the determination of six pyrethroid insecticides residues in aquaculture seawater via GC-ECD coupled with MISPE was evaluated.

2. Experimental

2.1. Chemicals

Fenvalerate (FEN), deltamethrin (DEL), cypermethrin (CYP), cyfluthrin (CYF), phenothrin (PHE), and bifenthrin (BIF) (Fig. 1) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Methacrylic acid (MAA) was obtained from Sigma–Aldrich (Steinheim, Germany), and the cross-linker ethylene glycol dimethacrylate (EGDMA) was from Fluka (Steinheim, USA). The initiator, 2,2′-azobis(2-isobutyronitrile) (AIBN), was purchased from the China National Pharmaceutical Group Corporation (Shanghai, China), and HPLC grade acetonitrile and methanol were from Fisher Scientific Co. (USA). All other reagents were of analytical grade. The aquaculture seawater samples were collected in a clean plastic bucket and passed through 25 mm diameter Whatman GF/C filters.

2.2. Polymer synthesis

The MIPs were synthesized via bulk polymerization. The DEL or CYP template (1 mmol) was dissolved in acetonitrile/acetone (9:1, v/v, 10.0 mL). The functional monomer (MAA, 4 mmol), the cross-linker monomer (EGDMA, 20 mmol), and the initiator (AIBN, 90.0 mg) were then added. The mixture was sonicated for 10 min under a N_2 atmosphere and then placed in a water bath at 60 °C for 24 h. After polymerization, the polymers were crushed and passed through a 50 μm sieve. The fine particles were further removed via sedimentation in acetone. The template molecules were extracted with methanol/formic acid (9:1, v/v) via Soxhlet extraction until the template molecules were undetectable by GC-ECD, and thermal annealing of the polymers was conducted at 120 °C for 6 h. Non-imprinted polymers (NIPs) were similarly prepared except for the absence of a template.

2.3. Adsorption capacity

The adsorption capacity of the MIPs and NIPs were obtained via batch rebinding experiments. In the binding assay, polymer particles (15.0 mg) were added to a 1.5 mL acetonitrile/acetone (9:1, v/v) solution of pyrethroid insecticides in various concentrations (from 0.25 to 1000 mg L^{-1}) and incubated for 24 h with stirring at 25 °C. The polymers were then removed via filtration, and the solutions were evaporated to dryness under a N_2 atmosphere and redissolved with 0.5 mL isooctane/acetone (9:1, v/v) followed by GC-ECD analysis. Three replicate binding assays were performed for each concentration. The amounts of rebound pyrethroid insecticides [B] were calculated by subtracting the amount of free pyrethroid insecticides [F] from the initial amount. Scatchard analysis was performed using the Scatchard equation [18].

2.4. BET analysis

The polymer pore parameters and surface areas were measured using a Micromeritics ASAP 2020 analyzer (Norcross, GA) and analyzed using the Brunauer–Emmett–Teller (BET) method. A 500.0 mg sample of the dried polymers was degassed at 150 °C for 24 h under a N_2 flow approximately 12 h prior to measurement. The N_2 adsorption/desorption isotherms were recorded at 77 K. The Barret–Joyner–Halenda (BJH) method was applied to acquire the pore size distribution.

2.5. MISPE

The MISPE column was prepared by packing 30.0 mg MIPs or NIPs into 3.0 mL SPE cartridges (Supelco, USA) with two frits at each end. First, the MISPE cartridges were sequentially preconditioned with 10.0 mL acetonitrile and 2.0 mL 20% acetonitrile in water prior to sample loading. Afterward, the cartridges were dried under a N_2 stream. Each cartridge was eluted with 3.0 mL acetonitrile/formic acid (9:1, v/v) at 0.5 mL min^{-1}. Finally, the elution fractions were dried under a gentle N_2 stream, redissolved in 1.0 mL isooctane/acetone (9:1, v/v), and then filtered through a 0.22-μm nylon filter for subsequent GC-ECD analysis.

Table 1
Binding characteristics of C-MIPs and D-MIPs.

	High-affinity binding sites		Low-affinity binding sites	
	K_d (μmol L^{-1})	B_{max} (μmol g^{-1})	K_d (μmol L^{-1})	B_{max} (μmol g^{-1})
C-MIPs	33.89	7.30	666.66	32.66
D-MIPs	15.55	3.19	416.66	17.95

Table 2
Comparison of the pore structural characteristics of the MIPs and the corresponding NIPs (means ± SD, n = 3).

Polymers	Surface area (m^2 g^{-1})	Total pore volume (cm^3 g^{-1})	Average pore diameter (nm)
C-MIPs	328.0 ± 1.4	0.58 ± 0.01	7.28 ± 0.06
D-MIPs	320.0 ± 1.7	0.55 ± 0.01	7.10 ± 0.04
NIPs	311.6 ± 1.5	0.52 ± 0.02	6.55 ± 0.05

2.6. Extraction of pyrethroid insecticides from aquaculture seawater via Florisil-SPE

The Florisil-SPE cartridges (6 mL, 200 mg, CNWBOND, Germany) were stacked onto a vacuum manifold and used for pyrethroid insecticides analysis [19]. The cartridges were initially cleaned with 5 mL methanol and then conditioned with 3 mL water. The filtered aquaculture seawater samples were pumped through the Florisil-SPE cartridges at a flow rate of 1.0 mL min^{-1} and washed with 3 × 1 mL water. The Florisil-SPE cartridges were then dried under a N_2 atmosphere. The analytes were eluted into a concentrator using 8.0 mL diethyl ether:acetone:hexane (2:2:1, v/v/v) at a flow rate of 2.0 mL min^{-1}. Finally, the elution fractions were dried under a gentle N_2 atmosphere, redissolved in 1.0 mL isooctane:acetone (9:1, v/v), and then filtered through a 0.22 μm nylon filter for subsequent GC-ECD analysis.

2.7. GC analysis

The samples were analyzed via GC-ECD using a GC-2010 gas chromatograph (Shimadzu, Japan) with a Supel SPB-5 capillary column (30 m × 0.25 mm I.D. × 0.25 μm film thickness). Nitrogen was used as the carrier and makeup gas at a flow rate of 1.0 mL min^{-1}. The standard solutions and sample extracts (1.0 μL) were injected in split mode with a ratio of 30:1 at an injection temperature of 240 °C. The oven temperature was programmed at 240 °C for 3 min, then raised to 290 °C at 5 °C min^{-1} and held for 5 min. The ECD temperature was set at 320 °C.

3. Results and discussion

3.1. MIP preparation and characterization

MISPE, as an application of MIPs, is used in the enrichment and cleanup of pollutants because of its higher specific affinity compared with that of conventional SPE. The adsorption capacity is an important factor that affects the separation and purification capability of an SPE sorbent. Therefore, to investigate the binding performance of the MIPs synthesized with DEL (D-MIPs) and CYP (C-MIPs) as templates, the binding affinity capacity of the polymers were evaluated via equilibrium binding experiments. Fig. 2 shows that the D-MIPs and C-MIPs exhibited higher affinity than the corresponding NIPs. The Scatchard plot was nonlinear, and two straight lines fit the Scatchard equation. The plot indicates that the MIP binding sites were heterogeneous with respect to the affinity of MIP for the corresponding template. Two types of distinct binding sites, namely, the high-affinity and low-affinity binding sites, with specific binding properties, were present in the MIPs. Under this assumption, the dissociation constants (K_d) and their corresponding B_{max} values for the high-affinity and low-affinity binding sites are summarized in Table 1. These results demonstrate that the prepared MIPs have selective adsorption and recognition capabilities. Furthermore, C-MIPs exhibited a higher K_d and B_{max} values than D-MIPs. BET analysis was conducted to further elucidate the physical and recognition properties of the polymers. The results were presented in Table 2. The MIPs have larger surface area, total pore volume, and pore diameter than those of corresponding NIPs, and C-MIPs exhibited the largest surface area and cavities, which

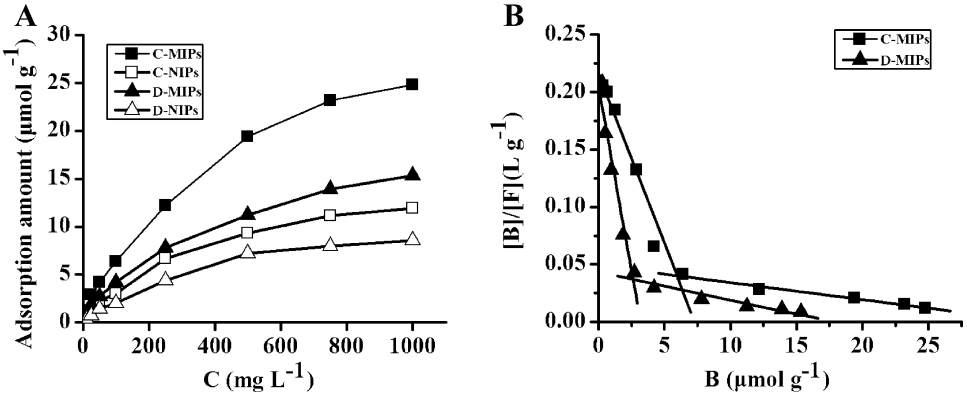

Fig. 2. Adsorption equilibrium isotherm (A) and Scatchard plot analysis (B) of MIPs and NIPs. Binding solvent, acetonitrile/acetone (9:1, v/v); equilibrium time, 24 h; C, initial analyte concentration.

Table 3
Percent recoveries of the pyrethroid insecticides obtained using different loading volumes spiked with 0.05 μg each of BIF, CYF, CYP, FEN, and DEL and 0.5 μg of PHE; $n = 3$.

Types	Volume (mL)	Recovery (%)						RSD (%)					
		BIF	PHE	CYF	CYP	FEN	DEL	BIF	PHE	CYF	CYP	FEN	DEL
C-MIPs	20	91.4	88.3	92.0	100.9	100.5	99.0	5.8	6.7	6.6	3.8	9.3	5.5
	40	90.4	87.2	91.7	99.3	96.5	96.1	5.1	6.5	4.3	5.5	4.9	4.0
	80	87.5	86.5	89.3	92.7	89.5	88.8	5.9	6.8	5.3	6.5	5.3	6.4
	100	89.2	86.8	85.8	90.8	88.1	86.3	5.5	4.2	5.8	6.0	5.3	5.9
D-MIPs	20	84.9	81.8	86.4	90.6	91.8	90.9	5.7	7.7	7.5	3.2	4.2	5.6
	40	84.8	82.7	87.0	91.7	90.2	89.7	4.3	7.5	4.3	3.9	4.5	6.9
	80	81.0	80.5	83.4	86.9	85.6	89.4	4.3	9.0	3.3	4.6	5.0	7.2
	100	76.2	75.7	81.7	82.3	80.7	82.1	7.0	4.8	5.6	4.5	3.3	6.4
Florisil-SPE	20	76.0	74.5	80.8	80.2	85.1	88.1	6.8	6.3	8.0	6.4	4.9	4.1
	40	78.5	60.5	66.3	69.8	74.3	73.4	7.0	5.7	4.5	6.1	5.4	3.1
	80	63.4	54.6	66.2	73.5	74.8	75.6	7.3	6.6	4.4	5.5	4.3	6.2
	100	63.7	54.5	56.3	59.0	52.9	55.8	4.7	8.4	6.4	7.6	7.6	5.5

are consistent with the results of the equilibrium rebinding experiments. The results indicated that increased surface and cavities in MIPs is likely due to the presence of the template molecule during polymerization and the difference in template.

3.2. Evaluation of MIP selectivity

MIPs are synthetic polymers with molecular recognition sites that can specifically rebind to the template and to a group of structurally related compounds when used in rebinding studies in appropriate solvents [20]. More recently, template shape and the functional groups in the template have been reported to play vital roles in molecular recognition by discriminating between different analytes [21,22]. In particular, when the analyte is much larger than the imprinted template, steric exclusion distinctly reduces the imprinting effect [23]. Fig. 1 depicts the structure of pyrethroid insecticides with a common chemical structure in that they contain cyclopropane carboxylic acids, but with different side chain group sizes and shapes [24]. Especially, the oxygen atom of carbonyl group in ester group of pyrethroid insecticides have a high electron affinity, which can form hydrogen bond with functional monomer of MAA [25–27]. Therefore, the group-selective characteristics of the C-MIPs and D-MIPs for pyrethroid insecticides were analyzed via MISPE.

A 1.0 mL solution spiked with 0.05 mg L^{-1} each of the six pyrethroid insecticides was percolated through MIP and NIP cartridges. The cartridge was then washed with 1.0 mL hexane as the initial washing solvent. The same experiments were performed using the NISPE cartridges. The results are shown in Fig. 3A. FEN, DEL, CYP, and CYF exhibited higher recoveries on the C-MIP (C-MISPE) and D-MIP (D-MISPE) cartridges than on the NISPE cartridges. By contrast, BIF and PHE both showed low recoveries on the MISPE and NISPE cartridges. These results clearly show that hexane can effectively disrupt non-specific binding. The structural

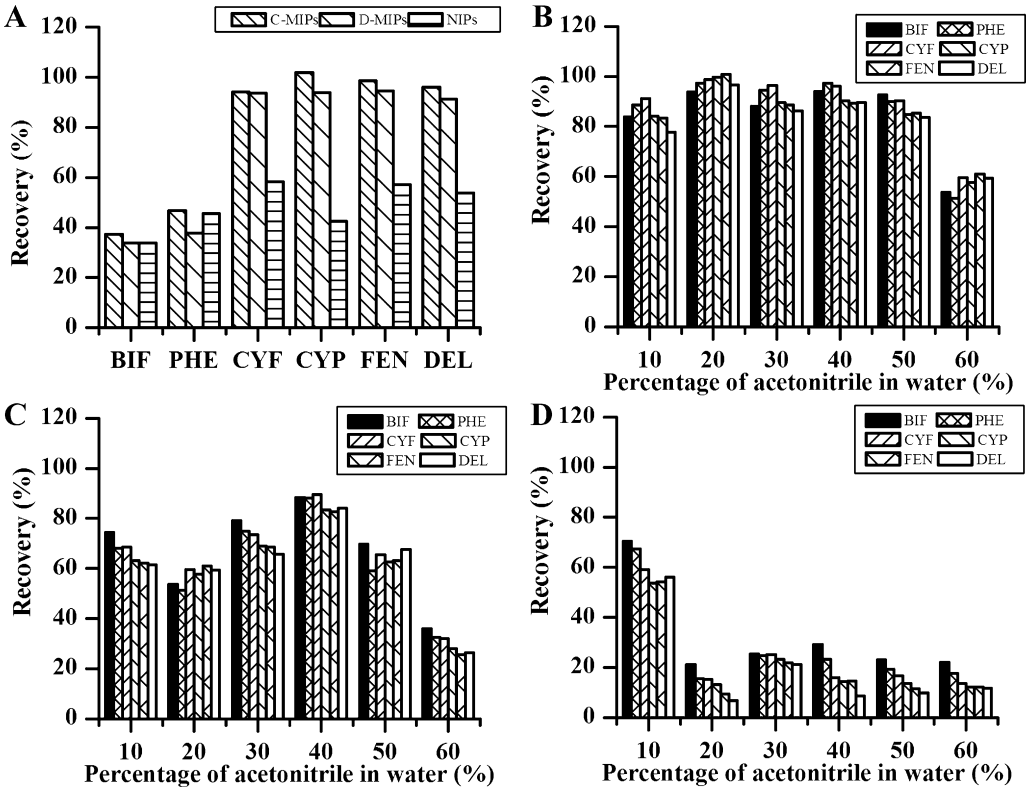

Fig. 3. Recoveries of the pyrethroid insecticides on MIPs and NIPs using different solvents as the washing solution: (A) using hexane as the washing solution; (B) on C-MIPs; (C) on D-MIPs; and (D) on NIPs.

Table 4
Analysis of the pyrethroid insecticides in spiked seawater samples using C-MISPE, D-MISPE, and Florisil-SPE; $n = 3$.

		Spiked concentration					
		0.01 mg L^{-1}		0.05 mg L^{-1}		0.1 mg L^{-1}	
		Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
C-MISPE	BIF	90.6	4.2	89.2	5.3	86.8	3.2
	PHE	90.0	3.1	87.1	5.7	86.4	4.9
	CYF	91.1	5.8	88.0	2.4	90.7	5.4
	CYP	96.0	6.6	92.9	3.5	91.4	3.3
	FEN	92.1	4.9	89.3	7.8	87.6	2.7
	DEL	93.5	4.1	93.6	4.3	90.8	4.5
D-MISPE	BIF	83.4	3.3	81.2	4.1	79.9	4.2
	PHE	82.1	7.9	73.8	6.0	75.6	4.4
	CYF	85.0	7.4	81.2	3.5	82.9	6.9
	CYP	87.9	6.3	84.1	4.3	83.4	5.8
	FEN	83.6	5.1	77.8	5.5	81.2	2.9
	DEL	88.8	4.5	83.7	4.3	84.5	6.2
Florisil-SPE	BIF	80.6	8.1	69.1	5.2	60.5	5.4
	PHE	82.9	7.0	68.8	9.0	59.2	6.2
	CYF	85.6	8.0	70.9	4.9	62.0	6.3
	CYP	84.9	5.2	71.4	5.0	60.8	7.4
	FEN	83.1	4.5	71.6	6.1	59.4	8.5
	DEL	68.9	9.7	65.9	6.9	48.5	9.6

effects of the analytes on specific binding were observed during the binding procedure. Meanwhile, although DEL has a molecular structure very similar to that of CYP, with two bromine atoms instead of the two chlorine atoms, CYP exhibited stronger specific affinity to the C-MIPs or D-MIPs than DEL in hexane solution. The reason may be ascribed to the oxygen atom of carbonyl group in ester group of CYP have a higher electron affinity compared to that of DEL, which can form hydrogen bond with functional monomer of MAA [25–27]. Hence, the hydrogen bond between the MAA and the carbonyl group plays an important role in the process of recognition in hexane. At present, lower organic solvent consumption in isolation and purification methods is usually preferred. In addition, specific rebinding between MIPs and the analytes in aqueous solutions has been demonstrated [28]. The members of the pyrethroid family share a common core structure. The MISPE conditions were further investigated to acquire good sample preconcentration and group selectivity for the six pyrethroid insecticides. The conditions were optimized with increasing acetonitrile from 10% to 60% in water, which was used as the washing solution. The MIP cartridges clearly have higher extraction recoveries for the six pyrethroid insecticides than the NIP cartridges (Fig. 3B–D), indicating that the MIPs have high specific affinity for the template and for the group of structurally related compounds because of the imprinting effect. In addition, the six pyrethroid insecticides exhibited the highest extraction recoveries when the C-MIP cartridges were washed with 1.0 mL 20% acetonitrile in water, which is in accordance with the results obtained from the Scatchard plot and the physical characteristics analyses. Therefore, the C-MIPs were selected for the subsequent MISPE experiments and 20% acetonitrile in water was used as the washing solvent.

3.3. Enrichment of pyrethroid insecticides from aquaculture seawater

SPE provides a rapid and effective enrichment and purification method for water samples. Conventional SPE usually results in low enrichment capacity when the water sample is directly run through the cartridges. However, the specific recognition of the template or of structurally related compounds in aqueous-rich media by MIPs can be achieved by selective interactions, including hydrogen bonding, ionic interactions, and hydrophobic effects [29].

Pyrethroid insecticides are present in low concentrations in aquaculture seawater. ECD, one of the most sensitive GC detectors, shows good sensitivity to pyrethroid insecticides. However, positive errors may occur due to complex matrix effects. Therefore, sample enrichment and purification are necessary to reach the sensitivity and accuracy of GC-ECD. To evaluate the enrichment capability of the C-MISPE cartridges, D-MISPE and Florisil-SPE were simultaneously tested using loading solutions ranging from 20 to 100 mL at a flow rate of 1.0 mL min^{-1}. The final loading amounts of BIF, CYF, CYP, FEN, and DEL were all 0.05 μg. The final loading amount of PHE was 0.5 μg. The results are presented in Table 3. In contrast to the results obtained using D-MISPE and Florisil-SPE cartridges, the estimated recoveries of the six pyrethroid insecticides using the C-MISPE cartridges were higher and above 85.8% (RSD 5.8%), indicating that the six pyrethroid insecticides can be almost entirely adsorbed by C-MISPE. C-MIPs exhibited good enrichment capability and can potentially be used as a novel SPE group-selective adsorbent material for the detection of the six pyrethroid insecticides.

3.4. MISPE application on aquaculture seawater samples

Compared with the conventional Florisil-SPE, the developed MISPE exhibited an excellent performance, with shorter sample preparation time and lower organic solvent consumption. The reliability of MISPE was further evaluated on aquaculture seawater from a local aquaculture area. Blank sample experiments were performed, and the absence of detectable pyrethroid insecticides was confirmed via GC-ECD. The validation of the developed analytical method was conducted by evaluating the following parameters: linearity and linear range, accuracy, intra-assay and inter-assay precision, limit of detection (LOD), and limit of quantitation (LOQ). The linearity for C-MIPs was checked using matrix-matched calibration curves by extracting the spiked seawater samples containing 0.01, 0.05, 0.1, 0.25 and 0.5 mg L^{-1} of six pyrethroid insecticides. The results for the six pyrethroid insecticides show an excellent correlation coefficient ($r^2 > 0.9912$) in the 0.01–0.5 mg L^{-1} range.

The analytical results of precision (RSD) and accuracy of the method for the aquaculture seawater samples spiked with the six pyrethroid insecticides are summarized in Table 4. Compared with the D-MISPE and conventional Florisil-SPE methods, the highest

Table 5
LOD and LOQ for the pyrethroid insecticides in the seawater samples after MISPE and Florisil-SPE obtained via GC-ECD; $n = 3$.

Analytes	Types	LOD (ng L^{-1})[a]	LOQ (ng L^{-1})[b]
BIF	C-MISPE	16.6	55.3
	D-MISPE	17.2	57.3
	Florisil-SPE	52.8	176.1
PHE	C-MISPE	678.9	2262.9
	D-MISPE	694.8	2315.8
	Florisil-SPE	1312.3	4707.6
CYF	C-MISPE	27.6	91.9
	D-MISPE	28.0	93.4
	Florisil-SPE	59.5	198.4
CYP	C-MISPE	32.7	109.1
	D-MISPE	34.5	114.9
	Florisil-SPE	67.8	226.1
FEN	C-MISPE	19.3	64.2
	D-MISPE	19.5	65.0
	Florisil-SPE	41.7	138.9
DEL	C-MISPE	28.0	93.5
	D-MISPE	37.0	123.2
	Florisil-SPE	78.2	260.7

[a] S/N = 3.
[b] S/N = 10.

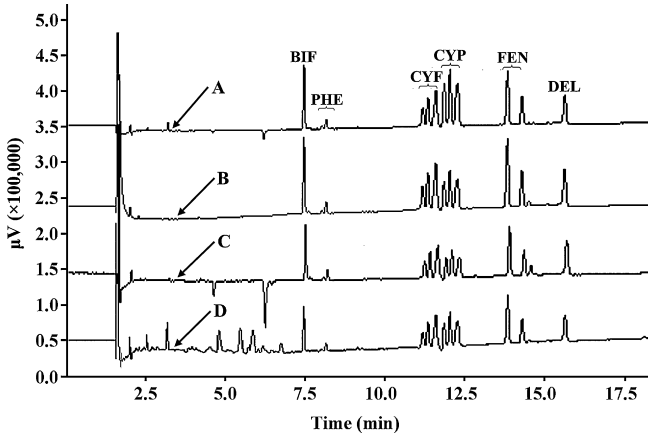

Fig. 4. Chromatographic profiles of 20 mL seawater samples spiked with 0.05 mg L^{-1} each of BIF (7.474 min), PHE (8.034 min, 8.167 min), CYF (11.021 min, 11.158 min, 11.361 min), CYP (11.568 min, 11.716 min, 11.908 min), FEN (13.175 min, 13.550 min), and DEL (14.627 min) after MISPE and Florisil-SPE: (A) reference standard; (B) spiked seawater samples after C-MISPE; (C) spiked seawater samples after D-MISPE; and (D) spiked seawater samples after Florisil-SPE.

mean quantitative recoveries acquired after C-MISPE are in the 86.4–96.0% range at three different spiked levels, namely, 0.01, 0.05, and 0.1 mg L^{-1}. The RSD values ranged from 2.4% to 7.8%, showing satisfactory robustness of the method in analyzing the pyrethroid insecticides in aquaculture seawater. The LOD and LOQ for the C-MISPE, D-MISPE, and Florisil-SPE methods were determined under optimum conditions, at signal-to-noise (S/N) ratios of 3:1 and 10:1, respectively. The results are shown in Table 5. The LOD and LOQ of five targeted pyrethroid insecticides in the seawater samples for C-MISPE were in the 16.6–37.0 and 55.3–109.1 ng L^{-1} ranges, respectively. PHE has higher LOD and LOQ, at 0.68 and 2.26 μg L^{-1}, respectively, than those of the other five pyrethroid insecticides. The considerable decrease in sensitivity for PHE is possibly due to the lack of halogen atoms in its molecular structure [29]. The typical GC-ECD chromatograms corresponding to the spiked aquaculture seawater samples following C-MISPE, D-MISPE and Florisil-SPE are shown in Fig. 4B–D, respectively. The peaks attributed to other matrix effects can be neglected in the spiked samples after MISPE. In addition, compared to the Florisil SPE cartridges, the developed C-MISPE exhibited lower consumption of organic solvent and better separation efficiency. These experimental results demonstrate that the MISPE method coupled with GC-ECD was successfully applied in the detection of the six pyrethroid insecticides in aquaculture seawater samples.

4. Conclusions

Group-selective MIPs for pyrethroid insecticides were prepared via bulk polymerization and subsequently applied to MISPE, which has higher selectivity and enrichment capability compared with conventional SPE. Subsequently, a novel preconcentration method based on MISPE, which has group selectivity for pyrethroid insecticides, and GC-ECD was developed and validated on the basis of linearity, precision, accuracy, LOD, and LOQ. The results demonstrate the excellent group-selective enrichment and purification performance of MISPE for the six pyrethroid insecticides at trace levels in aquaculture seawater samples.

Acknowledgments

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